3|RRTS

METHOD FOR PRODUCTION OF A PRODUCT HAVING SUB-MICRON PRIMARY PARTICLE SIZE, PRODUCT PRODUCED BY THE METHOD AND APPARATUS FOR USE OF THE METHOD

BACKGROUND OF THE INVENTION

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The purpose of producing metal oxides, metaloxy hydroxides, or metal hydroxides by using a sol-gel process is that these processes are simple low-cost processes, taking place at low temperatures. In these processes, it is possible to vary the production parameters, thereby obtaining a variety of product properties [Moran et al., 1999].

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By producing metal oxides, metaloxy hydroxides, or metal hydroxides in a traditional sol-gel process [Livage et al., 1998] an amorphous product is obtained with a finite particle size of 1 µm to 10 µm. In the traditional sol-gel process, it is necessary to calcine the product at high temperatures for up to 24 hours in order to obtain a crystalline product. In

15 addition to a higher energy-usage, this has the unfortunate effect within, for example catalysis applications, that the specific surface area is decreased by up to 80% [Andersen, 1975].

By using supercritical fluids as solvents in the sol-gel processes rather than the traditional

20 alcohols, a significantly lower particle size in the nanometer range can be obtained. This is believed to be due to the higher reaction rate obtained in supercritical media [Jung & Perrut, 2001].

Over the last decades the synthesis of ceramics and metal oxides in supercritical media

25 fluids (for example supercritical CO_2) has been further developed so as to improve upon the particle characteristics, for example in terms of chemical homogeneity and structure and morphology [Jung & Perrut, 2001].

The lowest temperature at which particulate material of the anatase phase of TiO_2 has

30 been produced in the prior art is 250 °C [Robbe et al. 2003]. This result, however, is obtained by first producing an amorphous TiO_2 under supercritical conditions and then calcining the amorphous product at 250°C.

The above mentioned process for producing the anatase phase at 250°C is based on a

35 patent [Sarrade et al., 2002], which describes the production of metal oxides and silicon oxides in a supercritical process. This process differs from the present invention in that it only yields amorphous oxides, which in order to become crystalline needs further calcination. These oxides have a particle size of 100 nm to 1000 nm.

A continuous supercritical production process [Reverchon et al. 2002] also results in amorphous nano-sized Titanium Hydroxide particles.

[Sievers and Karst, 1997] also describe a method for the supercritical production of 100nm
5 to 650 nm amorphous particles.

Yet another method for producing nano-sized metal oxides, metaloxy hydroxides, or metal hydroxides is by applying supercritical drying, where an already produced powder is inserted into a chamber, where it is dried in supercritical conditions by for example
10 supercritical CO_2. This process is described in [Yamanis, 1989], where different metal oxides are subjected to post-production supercritical drying, resulting in the obtainment of very large specific surface areas. This method also allows for the production of crystalline products without reducing the specific surface, as shown in [Yoda et al. 2001]. Yoda et al. demonstrate that the supercritical drying can increase the specific surface area of TiO_2 and
15 SiO_2 up to values of 700 -900m2/g.

Commercial crystalline TiO_2 is mainly made by flame oxidation synthesis of TiCl4 in a H2/O2 flame. An example of this is the commercially available Degussa P25 (Degussa GmbH, Germany) which has a particle size of ~ 35 nm and consists of a mixture of rutile
20 phase and anatase phase of TiO_2. Compared to the sol-gel process, it is difficult to vary the process parameters and thus the result, in flame oxidation synthesis [Brinker 1990]. In addition, it is not possible to produce a pure anatase phase, as it is less stable than the rutile phase. Flame synthesis is also used to produce, for example, silicon dioxide, alumina, and zirconium dioxide [Brinker, 1990]
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APPLICATIONS

As the above prior art suggests, nanoparticles, amorphous and crystalline, have received tremendous interest in recent years. This interest is spurred by the observation that many
30 properties of materials are radically altered with the inclusion of various forms of nanoparticles. Owing to the small volumes and the large surface-to-volume ratio, both electronic and physical characteristics of the materials can be strongly affected. For some characteristics it is important that the nanoparticle is amorphous, for others, that it has a certain crystalline phase.
35 An incomplete list of applications, in which metal-oxide nanoparticles can yield significant performance improvements is:

Chemical-mechanical polishing, Electroconductive coatings, Magnetic Fluid Seals, Magnetic recording media, multilayer ceramic capacitors, optical fibres, phosphors, quantum optical

devices, solar cell, antimicrobials, biodetection, biomagnetic separations, MRI contrast agents, orthopedics, sunscreens, automotive catalysts, ceramic membranes, fuel cells, photo catalyst, propellants, scratch-resistant coatings, structural ceramics and thermal spray coatings.

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Integration of metal oxide nanoparticles in some of these applications is already taking place at the industrial scale. However, for many applications the cost of nanoparticles is prohibitive, severely limiting the number of applications which can benefit. The general trend is for prices to rise as the size of the nanoparticles becomes smaller. Unfortunately it

10 is also a general trend, that it is the smaller nanoparticles that yield the largest improvement in performance.

BRIEF DESCRIPTION OF THE INVENTION

15 It may be an object of the invention to produce metal-oxide nanoparticles, by a method in which the total energy budget is minimised thereby reducing appreciably the cost of the final product.

It may furthermore be an object of the invention to produce metal-oxide nanoparticles, by

20 a method capable of inexpensively yielding very small nanoparticles that normally have a particular high price.

It may also be an object of the invention to produce metal-oxide nanoparticles, in which particle size, crystal phase, and degree of crystallinity can be controlled by external

25 parameters without having to resort to costly post-reaction processing.

In a first aspect, one or more of these and possible other object are achieved by a method of manufacturing a metal oxide, metal oxidhydroxide or metal hydroxide product, said product having a sub-micron primary particle size, comprising the steps of:

30 - introducing a solid reactor filling material in a reactor,
    - introducing a metal-containing precursor in said reactor,
    - introducing a co-solvent into the said reactor,
    - introducing a supercritical solvent into the said reactor,
    - establishing a contact between the metal-containing precursor and the co-solvent, thus

35 - resulting in the formation of said product in the proximity of the said solid reactor filling material.

In the context of the present application, the primary particles are the nano- or at least sub-micron particles that result from the formation. Usually these primary particles are

relative weakly bounded together in aggregates of particles. These aggregates can be considered as secondary particles. The scale of said proximity can be any scale ranging from an atomic level, a nano level, a micron level up to a macroscopic level.

5   Preferably, the formation takes place by a process involving a sol-gel reaction. The product obtained may either be substantially crystalline and substantially amorphous. In general, it may also be a combination of several different phases.

The method can be applied such that the introduction of the solid reactor filling material,
10 the metal-containing precursor, the co-solvent, and the supercritical solvent into the said reactor mayis done in any arbitrary order for easy and fast manufacturing.

Additionally, one of components: the solid reactor filling material, the metal-containing precursor, the co-solvent or the supercritical solvent, maymay be mixed with any of the
15 other components before introduction into the reactor. Furthermore, the method may be applied in a mode selected from the group of: batch mode, quasi-batch mode and continuos mode. This will be further elaborated in the detailed description.

The temperature in the reactor during the formation of said product is possibly kept at a
20 fixed temperature, but canmay also be performed at an increasing or a decreasing temperature, preferably with respect for the supercritical conditions to be fulfilled. Even alternatively, the temperature in the reactor may have a temperature profile consisting in an arbitrary selection of one or more fixed temperatures, one or more increasing temperatures and one or more decreasing temperature.
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The temperature in the reactor during the formation of the product is preferably maximum 400°C, more preferably maximum 300°C, even more preferably maximum 200°C, most preferably maximum 100°C, and even and most preferably maximum 50°C.

30 The pressure in the reactor during the formation of said product is possibly kept at a fixed pressure, but canmay also be performed at an increasing or decreasing pressure, preferably, with respect for the supercritical conditions to be fulfilled. Even alternatively, the pressure in the reactor may have a pressure profile consisting in an arbitrary selection of one or more fixed pressures, one or more increasing pressures and one or more
35 decreasing pressures.

Using carbon dioxide, as supercritical solvent the pressure in the reactor during the formation of the product should be as minimum 74 bar and the temperature in the reactor a minimum of 31°C. If one uses isopropanol as supercritical solvent, the pressure in the

reactor during the formation of the product should be as minimum 47 bar and the temperature in the reactor a minimum of 235°C.

5   The supercritical solvent may be supercritical before the introduction into the reactor or brought into a supercritical phase after the introduction into the reactor.

The present invention offers the astonishing possible, by means of a dedicated selection of the above process parameters, of producing anatase phase of TiO_2 already at temperatures as low as between 50°C and 100 °C and at concurrent pressures of 100-200 bar.

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The time of the formation of the product span the gap from maximum 0,5 hour to maximum 24 hours, depending on the number of process parameters, the number of process components and the one or more products for being produced by the process.

15 Preferably, a plurality of different metal-containing precursors may be introduced into the reactor opening up for a broader variety of alloys and possible doping of the product.

The metal-containing precursor may for example be a metal alkoxide, such as titanium tetraisopropoxide, titanium butoxide, titanium ethoxide, titanium methoxide, aluminium

20 isopropoxide, aluminium-sec-butoxide, or magnesium ethoxide.

The metal-containing precursor canmay be a metal salt, such as $Ti(SO_4)_2$, , $TiCl_4$ or $AlCl_3$.

Preferably, the co-solvent is selected from the group of: water, ethanol, methanol,

25 hydrogenperoxid and isopropanol, but a plurality of different co-solvents may also be introduced in the reactor.

The solid reactor filling material may function as a heterogeneous catalyst, preferably with a promoter.

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The solid reactor filling material may have various different forms, such as one or several fibres, a powder, and a substantially porous structure.

The solid reactor filling material may also have a size and shape capable of substantially

35 confining the metal-containing precursor to a limited part of the reactor. For example in form of a wad of fibres in top of the reactor confining the precursor to the top of the reactor, thereby separating the metal-containing precursor from the rest the reactor, e.g. a liquid in the bottom of the reactor. Alternatively, the solid reactor filling material has the shape from the group of a sponge, a grid, and a sheet.

The solid reactor filling material may comprise a polymer, such as polystyrene (PS), polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), or polyvinyl acetate (PVAc).

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Alternatively, the polymer is from the group of: acrylic polymer, fluorinated polymer, diene polymer, vinyl copolymer, polyamide polymer, polyester polymer, polyether polymer, or polyimide polymer.

10 The solid reactor filling material may also comprise a metal, such as titanium, aluminium, zinc, vanadium, magnesium, zirconium, chromium, molybdenum, niobium, tungsten, copper, or iron.

The solid reactor filling material may may comprise a metal oxide, such as titanium oxide, 15 zinc oxide, copper oxide, aluminium oxide, vanadium oxide, magnesium oxide, zirconium oxide, chromium oxide, silicium oxide, molybdenum oxide, niobium oxide, tungsten oxide, or iron oxide.

Preferably, the solid reactor filling material may comprise a ceramic, either natural or 20 artifical. Possibly, the solid reactor filling material comprises a metal sulphate or a metal halide.

The solid reactor filling material may function as seed material for the formation of the product. Preferably, the solid reactor filling material comprises a metal oxide, metal 25 oxidhydroxide or metal hydroxide identical to the product resulting from the formation in the reactor in order to initiate the formation of the product. The formation may for example also be by precipitation, catalysis, or growth. Alternatively, the solid reactor filling material functions as a collecting agent for the product.

30 The product is preferably separable from the solid reactor filling material with no further treatments of the solid reactor filling material. In this manner, the solid reactor filling material substantially does not degrade. Preferably, this allows the solid reactor filling material to be re-used as solid reactor filling material in a new formation step. The separation from the solid reactor filling material may take place by flushing the solid 35 reactor filling material in a fluid, by jolting, by vacuum means, by blowing means, or by ultrasonic means.

In comparison with known solutions in the art, e. g, exploiting nanostructured templates, the present invention is characterised by the fact that the sub-micron product is readily

separable from the reactor filling material without the need for plasma treatments, calcination or further chemical processing of the reactor filling material. Using e.g. nanostructured templates causes the product to be embedded within the template which necessitates a separation step that degrades the template. This is not the case with the

5 present invention.

In a second aspect the invention relates to a metal oxide, metal oxidhydroxide or metal hydroxide product manufacturing by the method of the first aspect of the invention, wherein the product is in the form of aggregates of primary particles with an average

10 primary particle size of in the range of 10-1000 nm.

In the presently most preferred embodiment the metal oxide product manufacturing by the method is TiO_2, preferably with a crystallinity of minimum 20%, preferably minimum 30%, more preferably minimum 40%, and even more preferably minimum 60% and even most

15 preferably minimum 80%. The titanium dioxide can be substantially crystalline anatase.

Alternatively, the metal oxide is from the group of: Al_2O_3, TiO_2, ZrO_2, Y_2O_3, WO_3, Nb_2O_5, TaO_3, CuO, CoO, NiO, SiO_2, Fe_2O_3 or ZnO.

20 More alternatively, the metal oxidhydroxide is from the group of: iron oxidhydroxide, titanium oxidehydroxide, manganese oxidhydroxide or aluminium oxidhydroxide.

Most alternatively, the metal hydroxide is from the group of: iron hydroxide, silicium hydroxide, zirconium hydroxide, titanium hydroxide, manganese hydroxide or aluminium

25 hydroxide.

A third aspect of the invention concerns an apparatus for manufacturing a metal oxide, metal oxidhydroxide or metal hydroxide product, said product having a sub-micron primary particle size, comprising the following components:

30 - means for introducing a solid reactor filling material in a reactor,
   - means for introducing a metal-containing precursor in said reactor,
   - means for introducing a co-solvent into the said reactor,
   - means for introducing a supercritical solvent into the said reactor,
   - said reactor intended as a space for establishing a contact between the metal-containing
35 precursor and the co-solvent and
   - said reactor intended as a space for the formation of said product in the proximity of the said solid reactor filling material.

BRIEF DESCRIPTION OF THE FIGURES

The invention is herafter described with reference to the following figures where

5   Figure 1 is a schematic illustration of the traditional sol-gel process where the particle size is a function of the reaction time after [Soloviev, 2000],

Figure 2 is a schematic drawing showing the generalized facility used in the supercritical sol-gel process according to the invention,

Figure 3 shows the crystalline phases of TiO_2, respectively brookite, anatase and rutile, as 10   a function of crystal phase formation temperature,

Figure 4 is a combined x-ray diffraction spectrum of the produced anatase TiO_2 powder and the expected location of anatase diffraction peaks,

Figure 5 shows the density of CO_2, having a low density at normal conditions, as a function of reduced pressure,

15   Figure 6 is an x-ray diffraction spectrum of a 50/50 weight ratio TiO_2 and CaF2 used to determine the crystallinity of the titanium dioxide powder as well as the crystallite size,

Figure 7 is a small-angle x-ray spectrum of an Al_2O_3 product produced by the present invention, used to determine the size of the primary particles,

Figure 8 is an x-ray diffraction spectrum of a 50/50 weight ratio TiO_2 (as produced by the 20   present invention) and CaF_2 used to determine the crystallinity of the titanium dioxide powder as well as the crystallite size,

Figure 9 is an x-ray diffraction spectrum of Al_2O_3 product produced according to the present invention showing clear diffraction peaks from the crystal structure termed Boehmite.

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DETAILED DESCRIPTION OF THE INVENTION

The invention, resulting in the production of nano-sized metal oxides, metaloxy hydroxides, or metal hydroxides, preferably makes use of a sol-gel process, in which a 30   precursor of a metal alkoxide or a metal salt is used. In the case of producing TiO_2 a precursor of a metal alkoxide may be e.g. titanium tetraisopropoxide, $Ti(OPr^i)_4$, titaniumbutoxide, $Ti(OBu)_4$, titaniumethoxide, $Ti(OEt)_4$, titaniummethoxide $Ti(OMe)_4$, or precursor of a metal salts may be e.g. $TiCl_4$, $Ti(SO_4)_2$.

35   The sol-gel process starts with the hydrolysis of the precursor, when it comes into contact with water. The hydrolysis continues simultaneously with the condensation of the hydrolyzed monomers leading to formation of nano-sized particles. The overall process can generally be expressed as follows [Livage et al., 1988]:

$$M(OR)_n + \tfrac{1}{2}nH_2O \rightarrow MO_{\frac{1}{2}n} + nROH$$
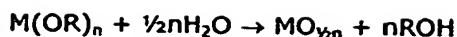
As an example, the total hydrolysis/condensation reaction can for the case of TiO_2 formation be expressed as

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$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH$$

The process must be controlled to obtain a desired structure and size of the final product. The colloid solution starts out as a sol. If the sol is stable, the solution will remain

10   unchanged. Often, however, a gelation or precipitation of particulate material takes place. Regardless of whether a sol, a gel, or a precipitate is formed, the product will, in the traditional sol-gel process, be dried and often calcined to obtain the final product.

A schematic illustration of the development of the particle size as a function of the reaction

15   time can be seen in Figure 1. It is seen that in the traditional sol-gel process a final particle size of 1-10 µm is obtained [Soloviev, 2000].

Utilizing a supercritical solvent (e.g. CO_2) can arrest the process shown in Figure 1. The supercritical solvent makes it possible to control and stabilize the particles such that the

20   particle growth is arrested before the steep part of the curve (in Figure 1) is reached, consequently resulting in nano-sized particles. By producing the particles in a supercritical fluid at specified process parameters and including a reactor material acting as seed or catalyst according to the present invention, it is furthermore possible to obtain partially or wholly crystalline products at relatively low temperatures.

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A supercritical fluid is used as a solvent in this process. A supercritical fluid is defined as a fluid, a mixture or an element, in a state in which the pressure is above the critical pressure (p_c) and the temperature is above the critical temperature (T_c). The critical parameters for selected fluids are shown in Table 1.

30

Table 1. Critical parameters for select inorganic and organic fluids [Jessop et al. 1999]

Inorganic Media	T_c [°C]	p_c [bar]	d_c [g/ml]
Ar	-122.5	48.6	0.531
CO_2	31.1	73.8	0.466
H_2O	374.0	220.6	0.322
SF_6	45.5	37.6	0.737
Organic Media	T_c [°C]	p_c [bar]	d_c [g/ml]
Methane	-82.6	46.0	0.163
Ethane	32.2	48.7	0.207
Propane	96.7	42.5	0.220
Hexane	289.5	49.2	0.300
Isopropanol	235.3	47.0	0.273
Ethanol	243.0	63.0	0.276

The characteristics of a supercritical fluid are often described as a combination of the
characteristics of gasses and those of liquids. As such, the supercritical fluid has the
viscosity of a gas and the density of a liquid. This makes them ideal as solvents in chemical
reactions. A comparison of these physical characteristics is shown in Table 2.

Table 2 General comparison of physical characteristics [Jessop et al., 1999]

Characteristic	Gas	Supercritical Fluid	Liquid
Density [g/ml]	10^{-3}	0,3	1
Viscosity [Pa·s]	10^{-5}	10^{-4}	10^{-3}

Due to the high density and the low viscosity the supercritical fluids are ideal for obtaining
high reaction rates as well as stabilizing and controlling the sol-gel process. This results in
the possibility of arresting the sol-gel process in Figure 1 and stabilizing the particles at a
size in the nano-regime of roughly 1-100 nm.

To enable the production and collection of nano-sized particles, a solid reactor filling
material is introduced in the production. These filling materials can act both as seed or
catalyst as well as a reservoir for collecting the nano particles. Examples of different filling
material are polymers, ceramics, metal fibres, and natural materials. The filling materials
can be coated and thereby have different surface properties such as hydrophilic or
hydrophobic surfaces. It is believed that the reactor filling material is especially helpful in
facilitating the formation of crystalline phases at low temperatures.

Equipment and Preparation

A generalized sketch of the equipment used to obtain the sub-micron product is shown in Figure 2. Central to this equipment is the reactor in which the product is formed under
5   supercritical conditions. The reactor is in general constructed such that both the temperature and the pressure can be controlled.

Both the metal containing precursor, the co-solvent, the solvent and the reactor filling material are introduced into the reaction chamber. The exact order of introduction and
10 circumstances under which these are introduced may vary substantially.

For example in one production route, which is considered to be an example of a pure batch route, the metal containing precursor, the co-solvent, and the reactor filling material may be introduced into the reaction chamber at room temperature and room pressure, albeit
15 separated in some fashion so as to not start the hydrolysis. Once the reaction chamber is closed, the temperature and the pressure can be raised to the supercritical level by either first raising the temperature, or raising the pressure or by some more complicated combination of the two. Raising the pressure may for example be performed as a direct result of introducing the solvent, in sufficiently large quantities.
20

In any combination of raising the temperature and the pressure, it is paramount that supercritical conditions are reached quickly. The solvent will transport the metal containing precursor and the co-solvent until they come into contact with each other, at which time hydrolysis will commence. After some time the chamber can be depressurized, cooled and
25 opened such that the reactor-filling material and the product which is located in proximity to the reactor filling material can be removed from the reactor.

In another example, which considered to be an example of a quasi-batch process, some of the components may be introduced into the reaction chamber at room temperature and
30 room pressure. For example, the reactor filling material and the metal-containing precursor, may be introduced at room temperature and room pressure. In such a quasi-batch process, the temperature and the pressure may be raised in arbitrary order, or perhaps following any number of more complicated temperature pressure routes. As in the above batch process the rise in pressure may happen as a direct result of the introduction
35 of the solvent or by any other means available in the prior art. To start the hydrolysis, it is necessary to introduce the co-solvent. This can be performed simultaneously with the introduction of the solvent, perhaps even mixing the solvent and co-solvent before introduction into the reaction chamber.

Alternatively, the introduction of the co-solvent can be performed well after the introduction of the solvent and well into the supercritical conditions. In this case the rate of hydrolysis can be controlled by the rate of co-solvent introduction into the reaction chamber. It is of course completely natural to rather consider the introduction of the
5 reactor filling material and the co-solvent at room temperature and pressure and to consider the later introduction of the metal-containing precursor and the solvent. One may also as a further extension of the semi-batch process consider only the reactor filling material to be placed in the reactor chamber in room temperature and room pressure conditions, and for the solvent, co-solvent and metal-containing precursor to be added
10 subsequently in preferably advantageous order and rates. After some time, the chamber can be depressurized, cooled and opened such that the reactor-filling material and the product can be removed from the reactor.

Finally, a continuous process is envisioned in which the reaction chamber is continuously
15 (or for very long times) maintained at supercritical temperature and pressure. In such a system the introduction and extraction of reactor filling material may be continuous, or quasi-continuous as for example if a load lock system capable of introducing and removing the reactor filling material to and from the reaction chamber, while in supercritical conditions, was available.
20

Such a load lock system may function by introducing the reactor filling material into the load lock, closing the load lock, bringing the load lock area to conditions comparable to those in the reaction chamber, opening a valve between the reaction chamber and the load lock, introducing the reactor filling material into the reaction chamber, letting the reaction
25 take place with the resulting product formed in proximity to reaction filling material, removing the reactor filling material from the reaction chamber into the load-lock, closing off the reaction chamber from the load lock, reducing pressure and temperature in the load lock, removing the reactor filling material (and the thereby the product) from the load-lock and subsequently taking steps to remove the product from the reactor filling materials by
30 one or more of the means above. With two such load lock systems, production may be almost continuous by utilizing alternating load lock to introduce the reactor filling material.

In the continuous process the introduction of respectively metal-containing precursor, co-solvent and solvent can take place in any number of imaginable combinations of rates and
35 routes to ensure the desired product characteristics.

In all of the above processing routes, one ends up with the product in proximity to the reactor filling material. In contrast to the prior art the process for separating the product from the fibre does not require a temperature treatment. In most cases it requires a

simple mechanical or dynamic manipulation to separate the product from the filling material. Examples of such manipulations can be flushing in a liquid, rubbing, shaking, vibrating, jolting, sucking e.g. use of vacuum, ultrasonically agitating etc.

5   It is a key feature of the invention and a prerequisite for obtaining reproducible results that the chemical sol-gel process takes place in a supercritical environment. It is assumed that the reaction in the supercritical environment together with the presence of reactor fill that enables the production of, for example, the meta-stable anatase phase TiO_2 at low temperatures without the need for after treatment.

10

Production Parameters and Associated effects

By changing the process parameters it is possible to vary the characteristics of the product. In the following table various process parameters and their influence on the end

15 product is listed.

Table 3. The influence of process parameters on the final product.

Process Parameter	Effect
Temperature	Crystalline phase and density
Pressure	Density
Reactant concentration	Particle Size
Amount of CO_2	Crystallinity
Reactor fill	Particle size and crystallinity
Additional supercritical drying	Crystallinity and surface area

20 It is seen in Table 3 that by changing the temperature, it is possible to vary the crystalline phases. The lowest possible process temperature would be the temperature required to obtain a supercritical state, which for CO_2 as the supercritical fluid is, 31.1 °C. Temperature has a significant influence on which phase of for example TiO_2 is produced. In Figure 3 the crystalline phases of TiO_2 is shown as a function of temperature. It is seen that the

25 commercially important phases of TiO_2 (anatase and rutile) normally are obtained at temperatures of respectively 350 -500 °C and over 900 °C [Stojanovic et al., 2000].

The pressure can also be varied, as long as the pressure is kept above the critical pressure that for CO_2 is 73.8 bar. By changing the pressure and temperature it is possible to change

30 the characteristics of the solution, in terms of density. The solvent density can have a great influence on the stability of a colloidal suspension as well as on the solubility parameters for the materials in the solution. From Figure 5 it is seen that CO_2 has a low

density at normal conditions (20°C and 1 bar), where CO_2 is a gas. Furthermore, it is seen that a significant increase in density is obtained near the critical pressure. Thus it is possible to fine-tune these parameters in order to obtain an optimal production environment.

5

In addition to changing the process parameters, the product can also be subjected to supercritical drying after the normal production process has taken place. Drying is done by opening valve V2 while still supplying the supercritical solvent fluid through value V1 at a given flow (F1) in a given time. The additional supercritical drying is expected to have an
10 effect on the crystallinity as well as on the specific surface area.

CHARACTERIZATION OF NANO PARTICLES

A solid can be considered as crystalline from a theoretical point of view if a Bravais lattice
15 can describe the structure of the solid. The crystallinity of the product produced by the present method is determined by x-ray powder diffraction patterns (XRD). The patterns can be recorded by any number of standard commercial diffractometers, but were in the present case recorded using a CuKα radiation (λ = 1.540 Å) from a STOE transmission diffractometer. The x-ray diffraction patterns are measured over a range of angles, which
20 for the present case ranged from 2Θ = 10° to 2Θ = 50° for TiO_2 samples and from 2Θ = 10° to 2Θ = 80° for AlOOH samples.

The crystallinity, as used in this document, is defined with respect to a 100 % reference sample, CaF_2, and the crystallinity is defined as being the background subtracted area of
25 the 100 % peak of the sample with unknown crystallinity divided by the background subtracted area of the 100 % peak of the 100 % crystalline CaF_2. The crystallinity ratio is compared to table values of the ratio between the respective peaks for a 100 % crystalline sample and CaF_2. The sample with unknown crystallinity and CaF_2 are mixed with a weight ratio of 50 %.
30

It is in the following shown how the crystallinity of a TiO_2 sample is determined. The ratio between the background subtracted area of the 100 % peak for anatase (101) and corundum in a 50 % weight ratio is:

$$\frac{A_{Anatase,101}}{A_{Corundum}} = 5.00$$

35 And the ratio between the 100 % peak of CaF_2 and corundum in a 50 % weight ratio is:

$$\frac{A_{CaF_2,220}}{A_{Corundum}} = 4.00$$

This gives a ratio between 100 % crystalline anatase and CaF_2 in a 50 % weight ratio is:

$$\frac{A_{Anatase,101}}{A_{CaF2,220}} = 1.25$$

This method can be demonstrated for Degussa P25 from Degussa GmbH, Germany, which is a commercial TiO_2 powder prepared by the flame oxidation synthesis and consists of

5 both the anatase phase as well as the rutile phase. The ratio between rutile (110) and CaF_2 is 0.85.

The sample is mixed in a weight ratio of 50% with CaF_2. The diffraction pattern for the determination of the crystallinity of Degussa P25 is shown in Figure 6. As shown on Figure

10 6 Degussa consists of both the anatase as well as the rutile phase of TiO_2. By analyzing the measured spectra from Degussa P25 powder and calculating the area of the peaks gives a fraction of 71 % crystalline anatase phase and 27 % crystalline rutile phase while the remaining 2 % is an amorphous fraction. This is in agreement with [Pozzo et al., 2002] who have measured the Degussa P25 powder to consist of 75 % anatase and 25 % rutile

15 and [Porter et al., 1999] who got 76.5 % anatase and 23.5 % rutile. [Porter et al., 1999] also report about an amorphous fraction in the Degussa P25 powder.

The x-ray powder diffraction patterns are also used to determine the crystallite size, τ, or primary particle size of the sample from Scherer's formula [Jenkins et al., 1996]:

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$$\tau = \frac{K \cdot \lambda}{\beta_\tau \cdot \cos\theta}$$

Where:

K = Form factor = 0.9

β_τ = Width of the peak at half the maximum intensity subtracted from instrumental noise

θ = Diffraction angle

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The crystallite size of Degussa P25 for the (101) peak is 35 nm.

The size of the primary particles, which can be different than the size of the crystallites determined above, can be determined by scanning electron microscopy (SEM) and Small-

30 Angle X-ray Scattering (SAXS).

The SAXS data can be obtained using any number of commercial or home-built systems, but in the present case was obtained using an adaptation of a Brukers AXS, Nanostar SAXS system, with a rotating anode x-ray generator, Cross-coupled Goebel mirrors and a Bruker

35 AXS Hi-star Area Detector.

The scattering intensity, I, was measured in terms of the scattering vector modulus

$q = 4n\sin(\Theta)/\lambda$, where $\lambda = 1.54$ Å. The scattering intensity was measured from $q = 0.0071$ Å^{-1} to $q = 0.334$ Å^{-1}. The data was corrected for background and azimuthally averaged to obtain a spectrum of average intensity vs. q. The data was then analyzed by fitting to the Beaucage model [Beaucage and Schaefer, 1994]:

$$\frac{I(q)}{I_0} = G \cdot \exp\left(\frac{-q^2 \cdot R_g^2}{3}\right) + B \cdot \left[\left(erf\left(\frac{q \cdot R_g}{\sqrt{6}}\right)^3\right)\bigg/q\right]^P$$

Where:

R_g: Radius of gyration

P: Mass fractal dimension

B: Pre-factor specific to the type of power-law scattering, specified by the regime in which the exponent P, falls

G: Classic Guinier pre-factor

The Beaucage model gives information of the size of the primary particle through the radius of gyration. The radius of gyration is defined as the weight average radius of the particles. In difference from XRD data SAXS can determine the size of primary particles of both crystalline as well as amorphous samples.

A Sorptomatic 1990 from ThermoQuest is used to determine the specific surface area of the produced powder. The apparatus measures the adsorption isotherm of nitrogen on the sample and calculates the surface area from this isotherm.

Example 1
Production of nano-sized TiO_2

In this example the production of nano-sized crystalline TiO_2 by a batch process is described. The precursor in this example is a 97 % titaniumtetraisopropoxide, $Ti(OPr^i)_4$, from Sigma Aldrich. It will in the following be referred to as TTIP. The TTIP reacts with distilled water in a supercritical environment including reactor filling material acting as seeds or catalyst material. The supercritical fluid is in this example CO_2. The experimental set up is shown in Figure 2 and the batch process is generically described in the Equipment and Preparation section.

The process equipment consists of a reactor where the supercritical sol-gel reaction takes place. The reactor in this example comprises reactor filling material in the form of fibres. The reactor is placed in an oven where the pressure and temperature can be controlled. The pressure can be changed from 1-680 bars depending on the desired product and is controlled by a pump (P1). The temperature can be changed from 25-250 °C and is

controlled by a temperature regulator (T1). The setup is a Spe-ed SFE-2 from Applied Separation Inc.

In the batch experiment the supercritical reactor is first filled with reactor filling material.
5 The TTIP is than injected in the top of the reactor into the reactor filling material and the water is injected in the bottom of the reactor into the reactor filling material. The amount of reactor filling material is adjusted as to prevent the reaction to take place before the $CO2$ is added to the reactor. The reactor is than placed in the preheated oven at 96 °C. The CO_2 is added immediately having an entering temperature of 1.3 °C and a pressure of
10 60 bar. The pressure is raised to the starting set point, 100 bar. The temperature in the reactor is reaching the set point in 30 minutes. As a result of the increasing temperature of the reactor, from room temperature to 96 °C, the pressure is increasing from 100 bar to approximately 170-200 bar in 30 minutes. The experimental parameters and the reactants amount for a standard experiment for TiO_2 is shown in table 4.
15

Table 4. Standard experiment

Temperature	Pressure	Reaction time	V_{TTIP}	V_{H2O}	Reactor filling material
96 °C	100 bar	4 hours	2.10 ml	1.00 ml	Hydrophilic PP

The amount of TTIP in a standard experiment is 2.10 ml and the amount of distilled water
20 is 1.00 ml that gives a hydrolysis ratio on 7.87. The filling material used is hydrophilic polypropylene polymer fibres (PP).

The standard experiment with the above process parameters has, according to the present invention, enabled the production of a pure anatase phase TiO_2. This is shown in Figure 4,
25 where an x-ray diffraction spectrum of a powder produced using the above equipment and method is shown. In the figure, the spectrum of the product is compared to diffraction lines expected from pure anatase. It is seen that except for broadening, which is due to the small size of the crystalline particle the observed lines coincide with those expected from anatase. No other TiO_2 phases are present. The crystallite size, τ, of this production
30 run has been determined to be approximately 10 nm. The following table shows the characteristic results of materials produced by the above preparation method and process parameters.

Table 5. Characteristics of TiO_2 powders produced by standard experiments

	Standard experiment
Crystalline phase	Anatase
τ [nm]	10.7 ± 1.0
Crystallinity [%]	40.0 ± 5.0
Particle size by SAXS [nm]	12.6 ± 1.0
Particle size by SEM [nm]	~ 20 ± 5
Specific surface area [m²/g]	236 ± 20

Table 5 shows that the result obtained by the present invention. The crystallinity of the
5 product is 40 ± 5 % over a series of 5 experiments. The remaining part is amorphous TiO_2.
The average particle size estimated by the crystallite size is 10.7 ± 1.0 nm. Both particle
size and crystallinity were derived from spectra like the one shown in Figure 8. The SAXS
measurement confirms that the powder consist of primary particle of 10-15 nm. The SEM
analysis also reveals that the samples are made out of nano-sized primary particles in a
10 range from 15-25 nm. These primary particles are then agglomerated into larger
aggregates. The BET measurement shows that the samples have a large surface area of
236 m²/g.

Example 1A
15 Production of TiO_2 with changing reaction times

In the following example the consequence of changing the process time is described. The
experiment is a standard experiment as described in example 1 but the reaction time is
changed. In the following table the influence of changing the process time is shown.
20

Table 6. Characteristics of TiO_2 powders produced at different reaction times

	2 hours	4 hours	8 hours
Crystalline Phase	Anatase	Anatase	Anatase
τ [nm]	8.5	10.7	10.7
Crystallinity [%]	39.5	40.0	39.4

By changing the reaction time the primary particle size changes slightly from 2 to 4 hours
25 but does not change from 4 to 8 hours. The increase of the reaction time does not result in
an increase of the crystallinity of the samples. The crystallinity is at all reaction times
approximately 40 %.

Example 1B

Production of TiO_2 at 43 °C

5   In this example a standard experiment is carried out as described in example 1 but the temperature is lowered to 43 °C. The results from this experiment is shown in table 7

Table 7. Characteristics of TiO_2 powders produced at 43 °C

	TiO_2
Crystalline phase	Amorphous
τ [nm]	-
Crystallinity	Amorphous
R_g [nm]	2.8

10

It is shown in table 7 that the powder is amorphous when produced at 43 °C. The size of the primary particles is determined by SAXS and is as low as 5.6 nm in diameter.

Example 2

15   Production of TiO_2 with different reactor filling material

In this example the influence of different reactor filling material is investigated. 5 different filling materials are examined and the influence on the product properties is determined. The reactor filling material is divided into 4 categories: polymers (in form of fibres),

20   ceramics (in form of small balls), metals (in form of steel wool) and natural material (a sheet of flax). Two polypropylene (PP) polymers with different surface properties are investigated.

Ten standard experiments, like those described in example 1, were carried out. Five

25   different reactor filling materials were used and the amount was adjusted separately. For each experiment the amount was determined so the reactants did not react before the supercritical CO_2 was added. In table 8 the results from these experiments are shown. The results are average values from the 2 experiments for each material.

Table 8. Measured properties of produced TiO_2 with different filling materials

	PP hydrophilic	PP hydrophobic	Ceramic	Metal fibre	Natural fibre
Crystal phase	Anatase	Anatase	Anatase	Anatase	Anatase
Crystallinity [%]	40.0 ± 5.0	32.4 ± 4.0	28.0 ± 5.5	25.7 ± 5.5	16.0 ± 4.0
Crystal size [nm]	12.4 ± 2.0	13.0 ± 2.0	13.4 ± 2.0	12.6 ± 2.0	18.5 ± 5.0

From table 8 it can be seen that the highest crystallinity comes from using the hydrophilic
5 PP as reactor filling material. It gives 40 % crystalline TiO_2 on anatase phase. The natural
material is not so applicable for producing crystalline TiO_2, only 16 % anatase phase. In
between is the hydrophobic PP, the ceramic and metal fibres. These 3 reactor filling
materials gives all around 25-33 % crystalline TiO_2 and because of uncertainties it is not
possible to distinguish between these 3 reactor filling materials regarding crystallinity. It
10 can also be seen that these 3 materials plus the hydrophilic PP gives the same crystal size
of 12.4 to 13.4 nm. The natural material gives a larger crystal size of 18.5 nm. The larger
crystallite size is due to bigger uncertainties in determining the peak parameters resulting
from a smaller peak. From the results in table 8 it is shown that using these 5 materials all
give crystalline TiO_2 at anatase phase.
15

Example 3
Production of Al_2O_3

In this example the production of nano-sized Al_2O_3 by a batch process is described. The
20 precursor in this example is aluminium-sec-butoxide, $Al(OBu^s)_3$, from Sigma Aldrich.
The hydrophilic polypropylene fibres are used as reactor filling material. The reactor filling
material, $Al(OBu^s)_3$ and water is placed in the reactor before inserting it in the oven and
the experiment is carried out as in example 1. In table 9 the process parameters and
reactant amount are shown.
25

Table 9. Al_2O_3 experiment

Temperature	Pressure	Reaction time	$V_{Al(OBus)3}$	V_{H2O}	Reactor filling material
96 °C	100 bar	4 hours	2.10 ml	1.00 ml	Hydrophilic PP

The reactant amounts give a hydrolysis ratio of 6.8. The produced material is nano-sized
30 and weak crystalline. The particle properties are shown in table 10.

Table 10. Characteristics of Al_2O_3 powders

	Al_2O_3
Crystallinity	Weak
R_g [nm]	9.7

The size of the primary particle is determined by SAXS measurement which yields a
5   diameter of 19.4 nm. The SAXS spectrum is shown in Figure 7.

Example 3A

Production of Al_2O_3 at 173 °C

10   In this example Al2O3 is produced at a higher temperature and hydrolysis ratio than
example 3. A batch process makes the production and the precursor in this example is
aluminium-sec-butoxide, $Al(OBu^s)_3$, from Sigma Aldrich.
The metal fibre is used as reactor filling material. The reactor filling material, $Al(OBu^s)_3$ and
water is placed in the reactor before inserting it in the oven and the experiment is carried
15   out like example 1. In table 11 the process parameters and reactant amounts are shown.

Table 11 Al_2O_3 experiment

Temperature	Pressure	Reaction time	$V_{Al(OBus)3}$	V_{H2O}	Reactor filling material
173 °C	100 bar	4 hours	0.96 ml	2.00 ml	Metal fibre

The reactant amounts give a hydrolysis ratio of 29.9. The produced material is nano-sized
20   and consists of the crystalline aluminium oxide hydroxide phase Boehmite. The
characteristics of the produced powder are shown in table 12 and the diffraction spectrum
is shown in Figure 9.

Table 12. Characteristics of AlOOH powders produced at 173 °C
25

	AlOOH
Crystalline phase	Boehmite
$\tau_{28.4°2\theta}$ [nm]	12.7
Crystallinity	93.5 %

The powder consists of 94 % crystalline Boehmite the main remaining part is amorphous
powder but the powder also consists of a small fraction of aluminium transitions

oxide/hydroxide phase. The crystals are 12.7 nm in dimensions determined by Scherrers formula.

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